



Influence of peroxide addition on the morphology and properties of polypropylene – multiwalled carbon nanotube nanocomposites



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ABSTRACT

The incorporation of peroxide as a reactive additive during the processing of polypropylene (PP) with multiwalled carbon nanotubes (MWCNTs) is investigated for its influence on the morphology, rheology, electrical, mechanical and thermal properties of the composites. PP is compounded with 2 wt.% of MWCNT in a twin-screw extruder with screw speeds of 500 and 1100 rpm. Additionally, PP modified with 1 wt.% peroxide is processed at 500 rpm with 1 and 2 wt.% MWCNT. Morphological investigations indicate better MWCNT dispersion in the composites at considerably lower specific mechanical energy (SME) input on peroxide addition. The decrease in complex melt viscosity on peroxide addition to PP is substantially compensated in the composites by the simultaneous enhancement in MWCNT dispersion. Electrical properties of the composites shaped by compression molding show at least three orders of magnitude higher conductivity than those obtained by injection molding. To detect electrical percolation, the composite granules from the compounding process were diluted to lower MWCNT contents using a small-scale melt mixer resulting in a threshold on compression molded plates at around 0.4 wt.%. Elastic modulus, tensile strength and notched impact strength of PP of the injection molded samples were slightly enhanced with MWCNT incorporation, but the effect of peroxide addition on these composite properties was rather negligible or negative. Thermal stability of PP was considerably enhanced on MWCNT addition and the composite with 1 wt.% MWCNT composite on peroxide addition showed thermal stability similar to that of the 2 wt.% MWCNT composite without peroxide. The finding that electrical and thermal properties achievable with 2 wt.% MWCNT incorporation in a widely used polyolefin like PP could be achieved with the combined effect of 1 wt.% MWCNT and peroxide at much lower SME highlights the significance of this investigation.

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1. Introduction

Achieving a good dispersion of carbon nanotubes (CNTs) in a polymer matrix is a significant step in realizing the attractive potential of CNTs as filler. In addition to being severely entangled due to their intrinsic van der Waals forces, the relatively high interfacial energies between CNTs and most polymers present a challenge to achieve optimum filler dispersion for improved macroscopic properties of nanocomposites. CNTs are theoretically expected to improve the mechanical and electrical properties when incorporated as fillers owing to their intrinsic characteristics. Significant progress has been made on the development of polymer–CNT composites especially with achieving good electrical

properties in thermoplastic [1,2] and thermosetting matrices [3,4] at low filler loadings. However, superior mechanical properties have been difficult to achieve principally due to the inability to achieve suitable nanotube dispersion and reinforcing polymer–CNT interfaces.

In thermosetting matrices, the low viscosity and ease of polymer melt penetration into the as-produced primary CNT agglomerates favors their disentanglement and present favorable conditions to achieve good CNT dispersion. In thermoplastic matrices melt mixing quite often performed using compounding is the preferred methodology for the production of polymer–CNT composites due to economic considerations and process flexibility. The process parameters (and consequently the shear stresses) have to be tailored to achieve an optimum dispersion quality within the extrudates [5–7], which eventually would be subjected to a subsequent shaping step, like injection molding, for the production of the final parts. Hence, optimization of the injection molding process to translate the achieved dispersion quality from the compounding

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step to desirable macroscopic properties is also critical. With both compounding and injection molding, there exists a potential trade-off of reduction in CNT aspect ratio [6,8,9] due to applied shear stresses for effective dispersion. Compression molding (another secondary processing step) however was reported to result in much higher electrical volume conductivity than injection molding [8,10], due to a less pronounced nanotube orientation especially in surface layers of the molded parts as well as, in most cases, longer holding time in the melt available for secondary nanotube agglomeration processes. However, it is important to understand the limitation of this technology towards large scale production of complex part geometries.

Polyolefins (POs) are the most attractive of the commodity thermoplastics due to their low cost and wide range of applications, but exhibit high interfacial energy difference with the CNTs which consequently results in poor dispersion and reinforcing behavior of CNTs. The electrical and mechanical property enhancements have been shown to be strongly hindered by inability to create a good CNT dispersion in POs, and hence higher CNT loadings are required for percolation as compared to those in polar thermoplastic composites containing CNTs [11–13]. Physical or chemical modification of CNTs is a strategy to adapt the CNT surface properties to those of the matrix or to create reactive bonds, respectively. The former is shown to aid good dispersion for low electrical percolation and high electrical conductivities [14,15] while the latter is expected to result in enhanced mechanical behavior [16,17]. In-situ polymerization of polyolefins in presence of CNTs is possible [18], but does not present a method which can be economically performed. Hence any effort to tailor dispersion should come from a functionality of the polyolefinic matrix, a modification of CNTs to be more non-polar and thus similar to POs, or from the aid of dispersing and stabilizing additives. The latter seems more practical and hence this directs our attention towards looking at possible additives during processing to improve the dispersion quality.

Peroxides are normally used in the industry for the viscosity control of the long chain polypropylene from the polymerization process. These peroxides induce degradation of the PP and function as an effective chain length modifier which in turns increases the melt flow rate (MFR) of PP. In addition, double bonds are formed which may be used for further reactions [19]. Peroxides have also reported to act as functionalizing agents for single walled carbon nanotubes (SWCNTs) [20]. This work is an attempt to study the effect of peroxide addition during the processing of PP with CNTs in a laboratory scale extruder and the observed effects on macroscopic properties of injection and compression molded composites. The effect of peroxide as a processing additive for a PP filled with multi-walled carbon nanotubes (MWCNTs) is discussed with focus on the morphological, rheological, mechanical, electrical, and thermal properties of the composites.

2. Experimental

2.1. Materials

Polypropylene grade R352-08R with a density of 0.9 g/cm³ (ISO 1183) and melt flow index of 8 g/10 min (ISO 1133) was purchased from DOW Chemicals. Nanocyl™ NC7000 grade purchased from Nanocyl S.A., Belgium was used as MWCNTs. According to the supplier these CNTs have a purity of 90%, an average diameter and length of 9.5 nm and 1.3 μm, respectively. PEROXAN BEC (t-butyl peroxy-2-ethylhexylcarbonate) from PERGAN GmbH, Germany was used as the source of organic peroxide. It is a liquid with a decomposition temperature of +60 °C. The raw materials were used as-received.

2.2. Processing

PP was introduced through the main feeding port of a Leistritz ZSE 27HP – 52D (Leistritz GmbH, Germany) twin-screw extruder with a screw diameter of 27 mm and an L/D ratio of 52 while the CNTs were introduced by adapting a side feeder at L/D = 16 to produce PP–MWCNT composites. Side feeding was performed as it was recommended in literature [21]. For the composites with peroxides, the liquid peroxide was premixed with the PP granules in a rotating batch mixer for 20 min and the mixture was fed at the main feeding port. Two screw speeds of 500 and 1100 rpm were used for PP/2 wt.% MWCNT composites, whereas for the composites containing 1 wt.% peroxide only 500 rpm could be used as at 1100 rpm the melt viscosity was too low to generate strands and pellets. Instead, a second sample with 1 wt.% MWCNT and 1 wt.% peroxide was produced for comparisons. The Specific Mechanical Energy (SME) of the compounding process in kWh/kg is given by:

$$SME = (2 \times M_{\max} \times I \times N) / (9550 \times E \times M) \quad (1)$$

where M_{\max} is maximum torque for one screw shaft (in Nm), I the motor current (in %), N the screw speed (in rpm), E the gear drive efficiency, and M the throughput (in kg/h).

Table 1 gives the nomenclature and processing conditions of the composites. The samples for tensile and impact testing were produced according to the dimensions governed by ISO 527-1 and ISO 179–1/1eA, respectively on an ENGEL ES 200/60 HL ST (ENGEL GmbH, Austria) injection molding machine. The injection molding parameters are presented in Table 2.

The composites C2-1100, C2-500 and C1-500-Px were subjected to melt dilution using a small-scale melt mixer MiniLab Haake Rheomex CTW5 (Thermo Scientific, Germany) under constant processing conditions (Table 1) to evaluate the electrical percolation thresholds on bars compression molded in a 4-stage process at different conditions, as listed in Table 2.

Compression molding of granules from extrusion and strands from the melt dilution process to samples of 60 × 10 × 1 mm³ was carried out on a Collins P 200 P/M (Dr. Collins GmbH, Germany) compression molding machine. Electrical conductivity of the composites processed by cooling the sample in the mold at rates of 10 K/min and 30 K/min did not show any differences in comparison to samples quenched in water (cooling rate of approx. 200 K/min); thus the latter approach was adopted in this work to minimize the cycle time.

2.3. Characterization of the composites

Optical microscopy (OM) was carried out in transmission mode on 5 μm thick slices cut perpendicular to the direction of flow on at least six different extruded strands employing a diamond knife with an R. Jung Microtome (Heidelberg, Germany). Imaging was done using 10× magnification objective lens of a BRESSER Science TRM-301 Transmission microscope (Meade Instruments Europe GmbH & Co. KG, Germany) fitted with a BRESSER Microcam. The area of visible MWCNT fraction (including all agglomerates with an area >20 μm² - or circle equivalent diameter >5 μm) to the total area of the optical micrograph is quantified to represent the undispersed MWCNT area fraction (A_f) and is taken as a measure of the quality of macro dispersion. A total area of 6 mm² was investigated according to the ISO 18553 norm for a descriptive statistic of A_f using the Image J software version 1.44o.

Contact angles for PP and peroxide modified PP (PP-Px) were evaluated with water and diiodo-methane as solvent drops using a Drop Shape Analysis (DSA) system from KRÜSS GmbH, Germany). The Owens–Wendt–Rabel–Kaelble (OWRK) method was used to calculate the surface tension of the solid PPs from these measurements and the known solvent parameters.

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